COMMUNICATION

A Zn_4L_6 capsule shows enhanced catalytic C-C bond formation activity upon C_{60} binding

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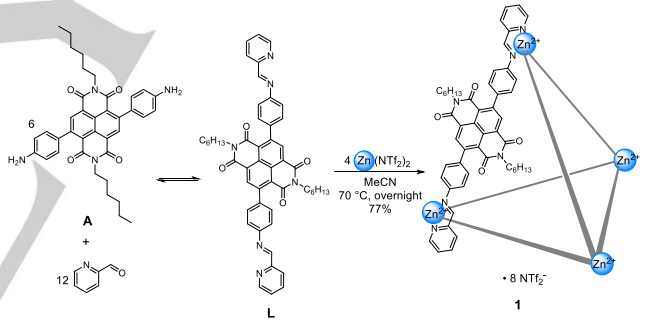
Abstract: A redox-switchable self-assembled $Zn^{II}_4L_6$ cage was synthesized that contains naphthalenediimide (NDI) motifs. Its reduction lent these NDI panels persistent radical anion character. The redox activity of this cage allows it to act as a catalyst for the oxidative coupling of different tetraarylborates to give biphenyls. The catalytic activity of the cage was enhanced following its binding of C_{60}, which implies a mechanism that does not involve encapsulation of the substrate.

The catalytic activity of enzymes can be regulated by the presence of chemical species other than their substrates.[1] Such regulation allows for complex chemical networks to be built up within living systems. The design of analogous abiological catalytic systems that can be regulated is an attractive goal for systems chemistry.[2] Artificial supramolecular catalysts are particularly well adapted to regulation,[3] and have proven useful in a wide variety of synthetic contexts.[4] Many metal-organic cages[5] have been developed as supramolecular catalysts,[6–17] where a substrate enters, is transformed, and exits again. Fujita and coworkers reported an early example of a Pd-based octahedral cage catalyzing the Diels-Alder reaction.[6] Recently Tiefenbacher and coworkers published a study of catalytic carbonyl-olefin metathesis through the combined action of HCl and a self-assembled supramolecular host.[7] Organometallic catalysts can also be introduced into assemblies to facilitate catalytic reactions by approaching the catalyst and the substrate.[18–22] For instance, by encapsulating a gold(III) complex, a Ga_4L_6 cage system could catalyze alkyl-alkyl reductive elimination.[18] Recently Reek and co-workers reported a self-assembled $M_{12}L_{24}$ sphere that contained inward-facing guanidinium groups that served as binding sites for both metal catalyst and substrates, leading to efficient catalysis.[21]

Here we demonstrate a novel mode of catalytic action for metal-organic cage, in which a co-catalyst, C_{60}, is encapsulated to enhance the catalytic activity. We infer the catalytic reaction, the oxidative transformation of tetraphenylborates into biphenyls, to take place on the surface of the cage, for reasons detailed below. This transformation is synthetically useful,[23] but greater interest is to be found in how it works: the cage serves to mediate electron transfer, without encapsulating the reaction's substrate. Naphthalenediimides (NDIs) have shown utility as catalytically active building blocks, for example by pre-organizing substrates by means of anion-π interactions.[24] NDIs can be reduced to form persistent radical anions,[25,26] which we hypothesized might mediate radical-induced reactions. NDIs[27] and related rylenes[28] have been successfully incorporated into functional cage structures *via* subcomponent self-assembly,[29] involving the thermodynamically-controlled formation of N=C and N→Metal linkages during a single overall synthetic process. We thus synthesized redox-switchable $Zn^{II}_4L_6$ cage **1** (Scheme 1) containing NDI moieties in its edges. This cage catalyzed oxidative-coupling reactions of organoborate compounds *via* a mechanism which we infer to involve its radical-anionic NDI panels.

Tetrahedral $Zn^{II}_4L_6$ cage **1** was formed from the reaction of 2-formylpyridine (12 equiv), NDI-containing diamine **A** (6 equiv) and $Zn(NTf_2)_2$ (4 equiv) in acetonitrile (Scheme 1). Its $Zn^{II}_4L_6$ composition was confirmed by NMR and ESI-MS analyses (ESI Figures S16–S25). Several sets of ligand peaks were observed by ^{1}H NMR, however all peaks corresponded to species that diffused at indistinguishable rates by DOSY-NMR (Figure S20). As observed in other M_4L_6 cages,[30] **1** thus appears to consist of a mixture of *T*, C_3 and S_4 diastereomers in solution, with **1**-S_4 predominating (Figures S21 and S50). The different diastereomers originate from differing ratios of Δ and Λ stereochemical configurations at the vertices. HSQC NMR (Figure S18) permitted the identification of peaks from the different diastereomers in solution, which clustered well in ^{1}H-^{13}C correlation space.



Scheme 1. The preparation of $Zn^{II}_4L_6$ cage **1**.

The redox behavior of **1** was investigated by cyclic voltammetry (CV). A quasi-reversible process involving two reductions was observed in 0.1 M nBu$_4$N$^+$Tf$_2$N$^-$ / MeCN at a scan rate of 300 mV s^{-1} (Figure 1). The first reduction wave appears at –1.1 V vs Fc/Fc$^+$; and the second reduction is found at –1.52 V vs Fc/Fc$^+$; both are attributed to the ligand NDI moieties.[31] When the one-electron reductant cobaltocene (Cp_2Co, 4 equiv) was added to **1** in CD_3CN, the ^{1}H NMR signal from **1** became broad (Figure S13), attributable to the paramagnetic nature of the new species.[26] The addition of excess tetrachloro-1,4-benzoquinone **4** (4 equiv) resulted in the recovery of the original cage (Figure S13), consistent with reversible reduction of the NDI panels of **1**. When more than 8 equivalents of Cp_2Co was added into a solution of **1**, a precipitate formed immediately, which we infer to result from charge neutralization, as the negatively charged panels compensated the cationic charges of the vertices.

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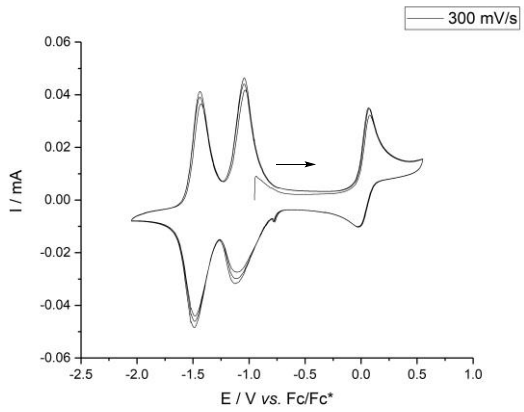


Figure 1. Cyclic voltammetry (three scans) of **1** in MeCN (0.1 M nBu$_4$N$^+$Tf$_2$N$^-$) at room temperature.

N-Methylfulleropyrrolidine **2** displays negligible solubility in MeCN. However, when heated in presence of cage **1**, this fullerene derivative became soluble. New ^{1}H NMR peaks corresponding to encapsulated **2** were observed at 3.25, 3.00 and 2.75 ppm, which were shifted upfield compared to free **2** in CS_2/$CDCl_3$,[32] consistent with the formation of a host-guest complex (Figures 2 and S6). When Cp_2Co was added into **2**⊂**1** in MeCN, the signals of the fullerene were still observed in the ^{1}H NMR spectrum despite broadening due to paramagnetism of the cage. This result shows the persistence of the cage framework following ligand reduction in the context of the host-guest complex with functionalized fullerene **2**.

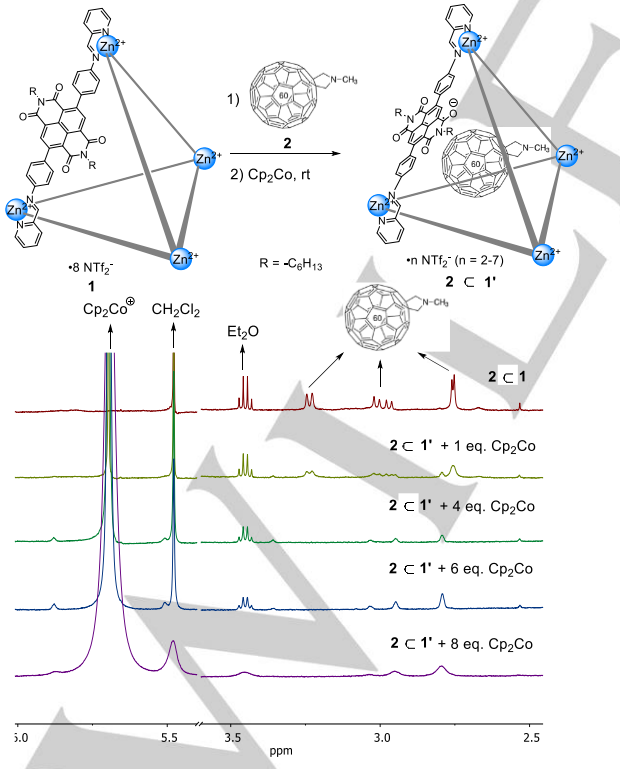


Figure 2. ^{1}H NMR (500 MHz) titration of Cp_2Co into a solution of **2**⊂**1** in CD_3CN. Precipitation was observed after the addition of 8 equivalents of Cp_2Co.

In addition to Cp_2Co, tetraarylborates also reduced cage **1** to produce radical species. Following the addition of potassium tetrakis(4-chlorophenyl)borate, the ^{1}H NMR of **1** became broad, and the color of the solution changed from yellow to dark brown. The EPR spectra of the solution confirmed the formation of a radical species (centered at g = 2.0041) (Figure S1). This reaction was accompanied by the formation of 4,4′-dichlorobiphenyl, which we inferred to derive from the boron radical intermediate **3a'** (Figure 3).[33] We thus set out to investigate the circumstances under which the redox-active cage **1** could serve as a catalyst for the oxidative coupling of organoborates (Figure 3).[23]

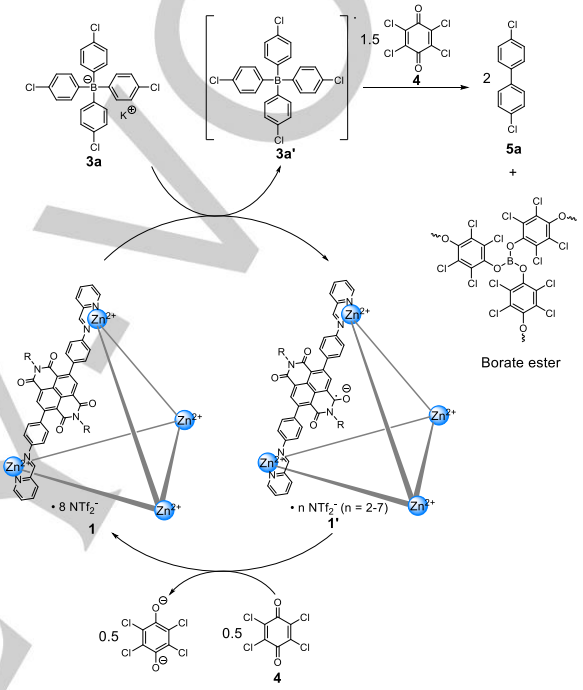
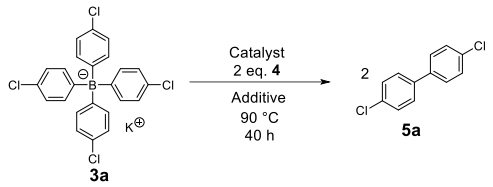


Figure 3. Proposed catalytic cycle for the oxidative coupling of organoborates mediated by cage **1**.

To explore this cage-mediated catalytic cycle, mixtures of potassium tetrakis(4-chlorophenyl)borate and tetrachloro-1,4-benzoquinone **4** were subjected to different catalyst loadings, and the presence or absence of the additive C_{60} (Table 1). We observed cage **1** to catalyze the formation of 4,4'-dichlorobiphenyl **5a** at 10% or 20% catalyst loading, but with less than 30% yield (Table 1, entries 1, 2, Figure S10). Upon addition of C_{60}, however, more than a two-fold increase of the yields was observed (entries 4, 5, Figures S9, S11), indicating that C_{60}⊂**1** is a more effective catalyst than **1** alone. C_{70} could also improve the catalytic efficiency, however less effectively than C_{60} (entry 6). When the C_{60}⊂**1** loading was further lowered to 5 mol%, a decrease in yield was observed (entry 3).

As control experiments, C_{60}, subcomponent **A** and its bis-formylpyridine condensation product **L** were tested independently as catalysts (entries 7-9). None of these produced more than traces of the product **5a**. A combination of **A** and $Zn(NTf_2)_2$ also did not generate **5a**, with chlorobenzene being formed (95%) instead (entry 10, Figure S12). We thus infer **1**, as opposed to its subcomponents, to mediate the catalytic reaction, and the host-guest interaction between C_{60} and **1** to promote the catalytic efficiency. This effect could be a consequence of stabilization of the radical form of **1**, as C_{60} is a known radical-stabilizing agent.[34]

Table 1. Optimization of the oxidative coupling of borate 3a



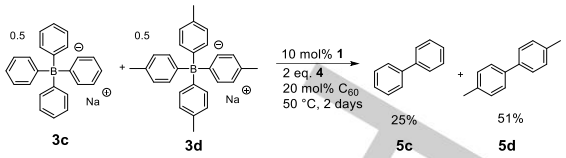
Entry	Catalyst	Additive	Yield/%[a]
1	10 mol% **1**	-	21
2	20 mol% **1**	-	28
3	5 mol% **1**	10 mol% C_{60}[b]	14
4	10 mol% **1**	20 mol% C_{60}[b]	56
5	20 mol% **1**	40 mol% C_{60}[b]	63
6	20 mol% **1**	40 mol% C_{70}	40
7	-	100 mol% C_{60}	0
8	100 mol% **A**	-	<5
9	100 mol% **L**	-	0
10	100 mol% (**A**+$Zn(NTf_2)_2$)	-	0[c]

[a] Yields were determined by ^{1}H NMR using pyrene as internal standard. [b] An excess of C_{60} was added to maximize the formation of $C_{60}\subset$**1** [c]Chlorobenzene was observed as sole product in 95% yield.

Following optimization, 10 mol% of $C_{60}\subset$**1**, was then used to explore the oxidative coupling of different borates. The examples shown in Table 2 indicate that this method tolerates both electron-withdrawing and -donating groups (entries 1-7). However, for electron-donating groups, a lower temperature was observed to improve the yield, with higher temperatures resulting in increased formation of protodeboronated mono-arenes as side products. Our method thus complements other catalysts, which perform best on tetra-arylborates bearing electron-donating groups.[35] Additionally, our method was applied to the synthesis of 2,2'-bi-naphthalene **3f** (entry 7), which is reported to require harsh reaction conditions for its synthesis.[36] Treatment of tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate with $C_{60}\subset$**1** (entry 8) did not lead to the corresponding biphenyl, which we attribute to the more strongly electron-withdrawing trifluoromethyl groups, which may prevent the borate from being oxidized by $C_{60}\subset$**1**.

Given that a higher reaction temperature was needed for the more electron-poor substrates (**3a**, **3b**), and that the ^{1}H NMR signals of cage **1** were observed throughout the catalytic process (Figures S10-S11), we infer that the reduction of $C_{60}\subset$**1** by borates into radical species is likely to be the rate-determining step. A proposed catalytic mechanism is presented in Figure S42. We note that encapsulation of C_{60} by **1** excludes borates from the cavity. Therefore, we infer that the radical catalytic reaction occurs on the surface of cage **1** rather than within the cavity (see Figure S41 and associated discussion in SI section 8.3).

To gain further insight into the catalytic mechanism, a mixture of **3c** and **3d** was treated with $C_{60}\subset$**1** (Scheme 2). Only the homo-coupling products **5c** and **5d** were obtained, consistent with the oxidative formation of biaryls from borates proceeding intramolecularly (Figure S49).

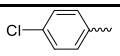
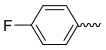
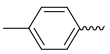
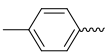
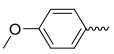
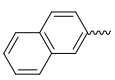
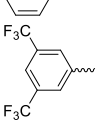


Scheme 2. Mixed substrate catalytic oxidative coupling reaction.

EPR experiments were carried out in order to clarify the nature of the radical intermediate of the catalytic reaction. The mixture of cage **1** with Cp_2Co (4 equiv) showed a broad EPR signal centered at g = 2.0040 (Figure S3), which is similar to the value observed for the borate reduced radical cage species (Figure S1). Following treatment with Cp_2Co, ligand L showed an EPR signal with a similar g value compared to cage **1** (centered at g = 2.0039), but with a distinct hyperfine coupling pattern (Figure S2), indicating that cage **1** did not decompose upon reduction. Interestingly, when C_{60} was encapsulated within **1** in the presence of **3a**, two sharp signals at 2.0016 and 2.0013, attributed to $C_{60}^{\bullet}$ species, were observed in the EPR spectra (Figures S4-S5),[37] suggesting that C_{60} is working as stabilizing agent by taking up some radical spin density.

In summary, a NDI-based redox-switchable self-assembled $Zn^{II}_4L_6$ cage has been developed as a catalyst for the oxidative coupling reaction of tetraarylborates. This catalyst has good functional group tolerance, and the mechanism of its action has been elucidated. Interestingly, either of the radical-stabilizing agents C_{60} and C_{70} was observed to act as a co-catalyst, binding inside the cage catalyst to enhance its catalytic activity. Further studies of this redox-switchable cage and its congeners as catalysts for other radical-induced reactions are under investigation.

Table 2. Scope of the catalytic oxidative coupling reaction

Entry[a]	3	Ar-Structure	T/°C	t/h	Yield/%
1	**3a**		90	40	56[b]/68[c]
2	**3b**		90	40	65[c]
3	**3c**		50	40	81[b]/62[c]
4	**3d**		50	40	62[b]/59[c]
5	**3d**		90	20	48[b]/64[c]
6	**3e**		50	20	71[b]/61[c]
7	**3f**		90	40	37[c]
8	**3g**		90	40	no reaction

[a] Standard conditions: 10 equiv borate, 1 equiv **1**, 20 equiv **4** and 2 equiv C_{60} were mixed in MeCN. [b] NMR scale (0.0014 mmol borate as starting material) determined by ^{1}H integration using pyrene as internal standard. [c] Isolated yield from larger scale (0.014 mmol borate as starting material).

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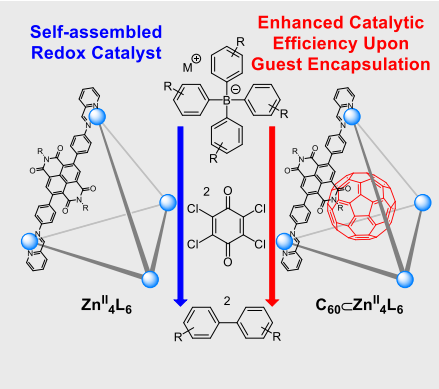
Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Buckyball in cage catalyst. A redox-switchable self-assembled $Zn^{II}_4L_6$ cage was synthesized that contains naphthalenediimide (NDI) motifs. The redox activity of this cage allows it to act as a catalyst for the oxidative coupling of different tetraarylborates to give biphenyls. The catalytic activity of the cage was enhanced following its binding of C_{60}, which implies a mechanism that does not involve encapsulation of the substrate.



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A Zn_4L_6 capsule shows enhanced catalytic C-C bond formation activity upon C_{60} binding